REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1/13/95	Final Ann. Tech. Rpt.; 11/1/91-10/31/94

4. TITLE AND SUBTITLE

Optimal Control of Molecular Motion

5. FUNDING NUMBERS

F49620-92-J-0076

61102F

2305/FS

6. AUTHOR(S)

Herschel Rabitz

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
Princeton University
Princeton, NJ 08544

8. PERFORMING ORGANIZATION REPORT NUMBER

AFOSR-TR· 95 - 0 0 9 7

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC NL
Building 410
Bolling Air Force Base
Washington, DC 20332-6448
Dr Michael R Berman

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DTIC
SELECTED
MAR 1 5 1994
F

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 words)

The overall objective of this research is to establish the physical principles for achieving control over molecular motion through the introduction of tailor-made optical fields. During the past year, this effort has involved both basic theoretical developments, as well as selected applications. Particular emphasis was given to establishing the robustness of laser field designs to various inevitable uncertainties and errors that may arise. In addition, an entirely new algorithm based on quantum mechanical tracking was introduced as a basis for a comprehensive treatment for both molecular control, as well as the inversion of controlled dynamics, to learn about the underlying Hamiltonians. The application of these various theoretical efforts was made to high quality ro-vibronic population inversion and the selective dissociation of HCN. Finally, a fundamental controllability algorithm was established, with the capability of assessing whether it is feasible to reach acceptable degrees of control in any particular molecule.

14. SUBJECT TERMS

Molecular Control, Quantum Mechanics, Optical Excitation, Data Inversion

15. NUMBER OF PAGES

9

16. PRICE CODE

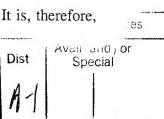| 17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
U	U	U	U

SUMMARY OF RESEARCH DEVELOPMENTS

Summarized below are the research developments which occurred during the previous year. Although each of the topics represents an independent study, they are all part of an overall fabric of theoretical research aiming to establish the foundations, and provide practical guidance for the laboratory achievement of control over molecular dynamical events.

1. **Optimal Control of Vibronic Population Inversion with Inclusion of Molecular Rotation.[1]**

    This work considered vibronic population inversion in the presence of molecular rotation. The objective was to invert the population of a vibronic level with populated rotational levels to a specific vibrational level in the excited electronic state, regardless of the detailed population distribution in the final rotational levels. The control of the multilevel population inversion was achieved by design of a pump pulse through optimal control theory. The total energy fluence and the pulse peak intensity were imposed as physical constraints in the design cost functional. A model diatomic molecule was used as an example, to investigate molecular rotational effects on the vibronic population inversion and the control properties, at different target times. The numerical results indicated that the shape-optimized pulses could achieve nearly complete population inversion, and largely overcome the difficulty that a rectangular pulse faces due to energy mismatches and multiple dipole transition moments.

2. **An Application of Minimax Analysis to Robust Optimal Control of Molecular Dynamics.[2]**

    Recent theoretical research has shown that a molecule can be manipulated and controlled by an optical field designed through optimal control theory. In practice, a number of disturbances/uncertainties arise, e.g., in the laboratory-generated control field, in the molecular Hamiltonian, or in the interaction term (i.e., the dipole moment). It is, therefore,

important to design an optimal control field which is robust to such disturbances. In this research, we applied minimax analysis to design optimal control fields in the presence of disturbances having finite magnitude. The minimax analysis sought the best control field in the presence of the worst disturbance of bounded magnitude; thus, the minimax solution gave a conservative estimate of the extent to which a physical objective could be achieved under the posed disturbances. As an example, we considered a diatomic molecule modelled as a Morse oscillator. The control objective was to achieve either selective excitation of a particular energy state, or to transform an initial wavepacket to an arbitrary non-stationary wavepacket, in the presence of the three aforementioned disturbances. For the former objective, the results for the bounded worst disturbances and robust optimal control fields were similar to those of previous perturbation calculations. For the second objective, however, the results significantly differed from analogous perturbation calculations. Under certain severe conditions, useful minimax solutions may be difficult to find, or simply do not exist.

3. **Robust Optimal Control of Quantum Molecular Systems in the Presence of Disturbances and Uncertainties.[3]**

Recently, systematic optimal control theory has been successfully applied to design optical fields which act on a molecule to guide or transform it into a specifically prescribed state. Under realistic laboratory conditions, and for real molecules, it is inevitable that there will exist disturbances and uncertainties in the control optical field, in the molecular Hamiltonian, and in the field coupling coefficient (e.g., the dipole moment), etc. Therefore, it is important to design an optimal field which is robust to disturbances. This work provided a method through which the worst possible disturbance to the control process, under certain possible constraints, could be calculated, and a corresponding optimal control field designed to be robust to the disturbances. Under disturbances of small amplitude a perturbation solution to

this problem could be applied. Illustrations were given for control of the wavepacket evolution of a diatomic molecule in the presence of disturbances.

4. **A Direct Method for the Inversion of Physical Systems.[4]**

In this work, a general algorithm was presented for the direct inversion of laboratory data to yield unknown functions in the underlying physical model. Of particular interest were linear and non-linear dynamical systems in chemistry and engineering applications. The potentially broad applicability of this method was examined in the context of a number of coefficient-recovery problems for systems described by partial differential equations. Stability issues were addressed, based on inverse asymptotic tracking. Numerical examples were presented, demonstrating the effectiveness of the algorithm.

5. **Tracking of Temporal Molecular Data: A Direct Inversion Algorithm for Recovering Potential Energy and Dipole Functions.[5]**

In this work, we presented a unified approach, based on the work of item 4. above, to invert molecular potential energy and dipole functions from time-dependent measurements. This algorithm combined time-dependent wavepacket propagation with the regularized solution of a Fredholm integral equation of the first kind containing the data. The result was a new non-linear, non-iterative algorithm to recover the potential and dipole functions from the time-dependent data. The recovered regions of these functions corresponded to those sampled by evolving wavepackets associated with the laboratory data. Although the algorithm was designed to track temporal data, synthetic tracking data may be generated for inversion by the use of appropriate steady measurements. This work, combined with the tracking control in item 9 below, forms a comprehensive approach to molecular control and laboratory data inversion.

6. **A New Approach to Molecular Classical Optimal Control:** **Application to the Reaction HCN → HC + N.[6]**

In this work, we presented a new method for classical control theory of Hamiltonian systems. This approach was based on a special treatment of the adjoint or Lagrange multiplier equations of motion. The latter function is only asked to preserve the mean of the ensemble of molecular trajectories. In this case, only four such equations are involved, greatly simplifying the field design process, and making it faster and more stable. Good results were obtained for the selective photodissociation of HCN. The objective was to control the intramolecular reaction HCN → HC + N (i.e., break the stronger bond). Hamilton's equations of motion were employed to model the HCN molecule, initially in its ground state. The control equations are integrated to obtain a high degree of selectivity in the unimolecular dissociation. The robustness of the results to changes in the initial conditions and pulse durations were investigated. An increase of the pulse duration beyond a certain point made it more difficult to dissociate the N atom, due to strong intramolecular coupling. The resultant pulse fields may serve as a basic indicator for future experimental selective dissociation of HCN → HC + N, using higher power lasers.

7. **Optimal Control of Classical Molecular Dynamics:** **A Perturbation Formulation and the Existence of Multiple Solutions.[7]**

This research considered the prospect for there being multiple solutions to the control of classically modelled molecular dynamical systems. The research followed up on a parallel study based on quantum mechanics. For polyatomic molecules, it is generally expected that a classical mechanical model will be adequate and necessary as a means for designing optical fields for molecular control. The prospect of multiple control field solutions existing in this domain was important to establish, in terms of ultimate laboratory realization of molecular control. A general formulation of the multiplicity problem was considered, and the existence

of a denumerably infinite number of solutions for the control field amplitude was shown to be the case under certain mild limitations on the physical variables.

8. Controllability of Molecular Systems.[8]

In this work, we analyzed the controllability of quantum systems arising in molecular dynamics. We modelled these systems as finite level systems, and examined their controllability. To do this, we passed to their unitary generators and used results on the controllability of invariant systems on Lie groups. Examples of molecular systems, modelled as finite-dimensional control systems, were provided. A simple algorithm to detect the controllability of a molecular system was provided. Finally, we applied this algorithm to a model five-level system.

9. Competitive Tracking of Molecular Objectives Described by Quantum Mechanics.[9]

This work further developed the basic concepts of inverse tracking for molecular control. The control of molecular events by optical fields was sought with the methods of asymptotic inverse tracking, local track generation (model matching), and competitive tracking, which are extensions of exact inverse tracking. The methodology was applied to infrared dissociation of a diatomic molecule, and selective dissociation of the stronger bond in a highly coupled linear triatomic system. The major appeal of these methods is that they do not require costly iterations, unlike other control approaches in which optimization techniques are used to design fields to achieve desired molecular objectives. It was found that in *exact* inverse tracking, where a requisite external field was obtained to exactly track a prescribed objective expectation value as a function of time, a high degree of intuition was required to find an *a priori* objective track, such that the required fields were reasonable in terms of intensity and bandwidth. Furthermore, exact inverse tracking does not allow for tracking of multiple observables. The extensions of the inverse tracking method presented in this study helped to alleviate these drawbacks. In all of these extensions, the requisite field was

computed locally in time, through minimization of a cost functional which contained terms designed to minimize the error between the objective and actual tracks, and also minimize the field fluence. The objective tracks could be prescribed *a priori*, as in exact inverse tracking or from the evolving system state (local track generation). Competitive tracking allowed for the following of multiple observables, although none were tracked exactly. Locally generated tracks (model matching) required less physical intuition because it was easier to specify an objective track with current knowledge of the state of the system. The concepts of molecular tracking form the key foundations of our inversion work in item 5 above.

PUBLICATIONS

1. Optimal Control of Vibronic Population Inversion With Inclusion of Molecular Rotation, L. Shen and H. Rabitz, *J. Chem. Phys.*, **100**, 4811 (1994).

2. An Application of Minimax Analysis to the Robust Optimal Control of Molecular Dynamics, H. Zhang and H. Rabitz, *J. Chem. Phys.*, **101**, 8580 (1994).

3. Robust Optimal Control of Quantum Molecular Systems in the Presence of Disturbances and Uncertainties, H. Zhang and H. Rabitz, *Phys. Rev. A*, **49**, 2241 (1994).

4. A Direct Method for the Inversion of Physical Systems, L.F. Caudill, Jr., H. Rabitz, and A. Askar, *Inverse Problems*, **10**, 1099 (1994).

5. Tracking of Temporal Molecular Data: A Direct Inversion Algorithm for Recovering Potential Energy and Dipole Functions, Z-M. Lu and H. Rabitz, *Phys. Rev. A*, submitted.

6. A New Approach to Molecular Classical Optimal Control: Application to the Reaction HCN $\rightarrow$ HC+N, J. Botina, H. Rabitz, and N. Rahman, *J. Chem. Phys.*, in press.

7. Optimal Control of Classical Molecular Dynamics: A Perturbation Formulation and the Existence of Multiple Solutions, M. Demiralp and H. Rabitz, *J. Math. Chem.*, **16**, 185 (1994).

8. Controllability of Molecular Systems, V. Ramakrishna, H. Rabitz, M.V. Salapaka, M. Dahleh, and A. Peirce, *Phys. Rev. A*, in press.

9. Competitive Tracking of Molecular Objectives Described by Quantum Mechanics, Y. Chen, P. Gross, V. Ramakrishna, H. Rabitz, and K. Mease, *J. Chem. Phys.*, submitted.

PROFESSIONAL PERSONNEL ASSOCIATED WITH
THE RESEARCH REPORT

1. Herschel Rabitz

2. Valery Dubov

3. Paul Mayer

4. Metin Demiralp